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Part IX

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PHASE EQUILIBRIA INVESTIGATION OF BINARY, TERNARY, AND HIGHER ORDER SYSTEMS

Part IX. Calculation of Thermodynamic Quantities
from Phase Diagrams

E. RUDY

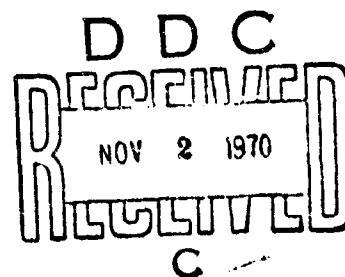
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FOREWORD

The research described in this technical report was carried out under USAF Contract F 33 615 -67-C-1513 by the Aerojet-General Corporation, Sacramento, California. This contract was initiated under Project No. 7350, Task No. 735001, and administered under the direction of the Air Force Materials Laboratory with Captain P. J. Marchiando (MAMC) as Project Engineer. Dr. E. Rudy, Aerojet-General Corporation (now at the Oregon Graduate Center, Portland, Oregon) was the Principal Investigator. This report forms the essential content of a paper presented by the author at the Symposium on Reprocessing of Nuclear Fuels, held at Iowa State University, Ames, Iowa, August 24-27, 1969.

This report covers work conducted during the period April 1967 through May 1969. It was submitted by the author in February 1970.

Other Reports issued, or in preparation, under USAF Contract AF 33 (615)-67-C-1513, have included:

- Part I. The Phase Diagrams of the Systems Ti-Nb-C, Ti-Ta-C, and Ti-Mo-C.
- Part II. Effect of Re and Al Additions on the Metal-Rich Phase Equilibria in the Ti-Mo-C and Ti-Nb-C Systems.
- Part III. Phase Studies in the V-Ta-C and Nb-Ta-C Systems
- Part IV. Effect of Mo and W Additions on the Subcarbide Solid Solutions in the V-Ta-C and Nb-Ta-C Systems.
- Part V. The Phase Diagram of the W-B-C System
- Part VI. The Phase Equilibria in the Metal-Rich Region of the Hafnium-Tantalum-Nitrogen System
- Part VII. The Phase Diagram Ti-V-C
- Part VIII. The Structure of a Ternary Phase T_3C_2 in the V-Ta-C System

This technical report has been reviewed and is approved.


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ABSTRACT

The thermodynamic fundamentals relating phase equilibria in binary and ternary systems to the thermodynamic properties of the phases are reviewed and discussed. Considered in detail are partition equilibria in ternary systems and the role of the three-phase equilibrium in the determination of the relative stabilities of stable as well as hypothetical phases.

Sample calculations carried out on selected ternary metal-carbon and a metal silicate system demonstrate the application of the equations for extracting thermodynamic data from phase diagrams and also for the prediction of phase equilibria.

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I. INTRODUCTION

The purpose of a constitution, or phase, diagram is to depict in condensed form the phases and their interrelationships in the given alloy system under chosen external conditions, such as temperature, pressure, etc. The information derived from the phase diagram is quantitative in respect to nature and composition of the coexisting phases at equilibrium and thus will also tell us, whether or not, or to what extent, given alloy mixtures will undergo reactions when heated to temperatures, and for times sufficient to allow equilibration.

The equilibrium state of a substance, which may consist of one or more phases, is characterized by a minimum of the free enthalpy G . Using this principle, the general relationships for the coexistence of phases under equilibrium conditions were formulated by W. Gibbs now almost a century ago and provided the basis for the interpretation of complex heterogeneous equilibria.

The value of the thermodynamic approach in the interpretation of phase equilibria was demonstrated by van Laar⁽¹⁾, who calculated binary phase diagrams using the regular solution approximation. These calculations were later extended to ternary solution systems, particularly by J. L. Meijering⁽²⁾. The law of mass action was applied to equilibria formed between liquid alloys and certain slags⁽³⁾, but a clear formulation relating the thermodynamic properties of boundary phases to the tie line distribution in a two-phase field was given only recently by Scheil⁽⁴⁾. Comparatively little effort was made in the past to establish explicit relationships for the calculation of ternary phase equilibria involving participation of crystallographically nonequivalent phases^(2,5). The following discussion is an attempt to summarize recent work in this field.

Although, owing mainly to the lack of adequate experimental data in other alloy classes, the sample calculations given in this report mostly refer to systems based on interstitial-type phases, the thermodynamic expressions have general validity and can be quite readily adapted for the description of systems of other phase types.

Before entering the discussion of ternary phase equilibria, let us consider a few essential points concerning the thermodynamics of binary systems.

Figure (1b) shows the principal course of the free energy in a binary system of isostructural components forming a miscibility gap. It is seen, that the phase relationships in such a system are solely governed by the thermodynamic behavior of the solution. The solubility limits are determined by the condition that the partial free energies of the individual components are the same at the boundary a_o and a'_o , i.e.,

$$\bar{G}_A(a_o) = \bar{G}_A(a'_o) \quad (1a)$$

$$\bar{G}_B(a_o) = \bar{G}_B(a'_o) \quad (1b)$$

These conditions implicitly contain the requirement for a common tangent to the free energy curve. The conditions for an eventually existing critical solution point x_c, T_c ($p = \text{const}$) are:

$$\left[\frac{\partial^2 \Delta G^{\text{mix}}}{\partial x^2} \right]_{T_c, x_c} = 0; \quad \left[\frac{\partial^3 \Delta G^{\text{mix}}}{\partial x^3} \right]_{T_c, x_c} = 0; \quad \left[\frac{\partial^4 \Delta G^{\text{mix}}}{\partial x^4} \right]_{T_c, x_c} > 0$$

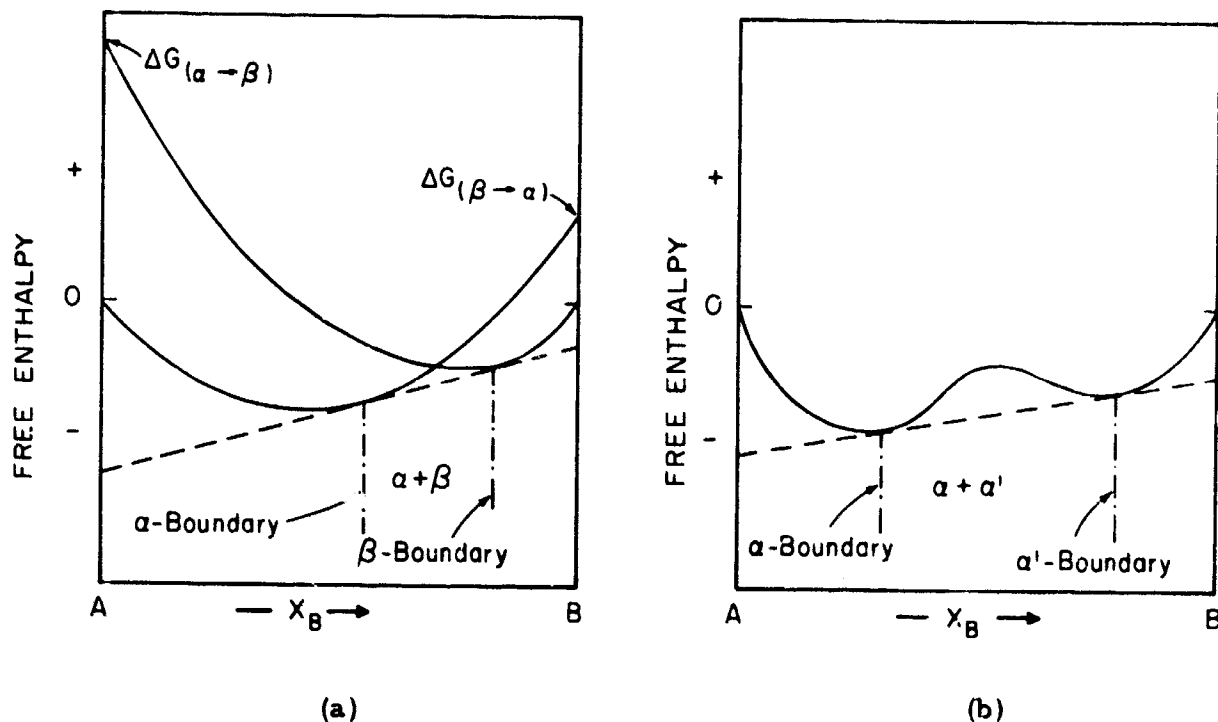


Figure 1. Free Enthalpy - Concentration Relationships in a Binary System of Non-isomorphous (a) and Isomorphous (b) Components, the Latter System Having a Miscibility Gap.

Of greater interest than the preceding type is a system formed by two components which differ in their crystal frameworks, Figure (1a). For such a system, in general, temperature-dependent mutual solubilities will be observed, but the two solutions will always be separated by a two-phase field of finite width. Such cases are exemplified, for instance, by the systems Mo-Ru⁽⁶⁾ (bcc-hcp), W-Pd⁽⁷⁾ (bcc-fcc), and in the systems Ti-Mo and Ti-V⁽⁸⁾ (hcp-bcc) below the transition point of titanium. The principal question which arises concerns the relationships between the magnitude of the atom exchanges in the two structurally nonequivalent lattices and the thermodynamic parameters of the system.

Let A and B be the constituents of such a binary, or pseudobinary system. The stable crystal modification of A may be designated by α and

that of B with β . $(A,B)_\alpha$ is then the solid solution having the structure α , and $(A,B)_\beta$ that of β . Without affecting the generality of the conclusions to be drawn, we may assume that no further intermediate phases are formed, i.e., the free enthalpies of other lattice type phases shall be more positive than those of $(A,B)_\alpha$, $(A,B)_\beta$, or any mechanical mixture of both.

We expect from the free enthalpy relationships shown in Figure (1a), that, apart from the effect of temperature, the adaptability of the lattice of each component to that of the partner will, in addition to the solution behavior, influence the widths of the homogeneous ranges, i.e. we expect the atom exchanges in both lattices to be linked to, and dependent on, the transformation energies $\Delta G_{(\alpha \rightarrow \beta)}$ and $\Delta G_{(\beta \rightarrow \alpha)}$.

To obtain a mathematical relationship between the compositions and the free enthalpies, we use as a starting point the well-known relation that at equilibrium the thermodynamic potentials of A and B must be the same at the homogeneity limits of both phases, i.e.

$$\overline{\Delta G}_{A(\alpha)} = \overline{\Delta G}_{A(\beta)} \quad (2a)$$

and

$$\overline{\Delta G}_{B(\alpha)} = \overline{\Delta G}_{B(\beta)} \quad (2b)$$

Denoting the integral free enthalpy of mixing of the α -phase with G^{mix} and that of B with G_β^{mix} , and using the stable modifications of A and B as the reference states, we obtain

$$\overline{\Delta G}_{A(\alpha)} = \overline{G}_{A(\alpha)}^{\text{mix}} \quad (3a)$$

$$\overline{\Delta G}_{A(\beta)} = \overline{\Delta G}_{(\alpha \rightarrow \beta)} + \overline{G}_{A(\beta)}^{\text{mix}} \quad (3b)$$

or, combining equations (3) and (3a) with the aid of equilibrium condition ():

$$\bar{G}_{A(\alpha)}^{\text{mix}} - \bar{G}_{A(\beta)}^{\text{mix}} = \Delta G_{A(\alpha \rightarrow \beta)} \quad (4a)$$

Analogous considerations for the component B yield:

$$\bar{G}_{B(\beta)}^{\text{mix}} - \bar{G}_{B(\alpha)}^{\text{mix}} = \Delta G_{B(\beta \rightarrow \alpha)} \quad (4b)$$

It is seen from equations (4a) and (4b) the extent of mutual solubility is not only controlled by the solution behavior, but also by the energy necessary to transform the lattice of one component into that of the partner. As an example, it follows from equation (4a), that $\bar{G}_{A(\beta)}^{\text{mix}}$ must be more negative than $\bar{G}_{A(\alpha)}^{\text{mix}}$, in order to counterbalance the positive term $\Delta G_{A(\alpha \rightarrow \beta)}$ on the right hand side of the equation, i.e. the component A is present in higher dilution [$x_{A(\alpha)} > x_{A(\beta)}$] in the β - than in the α -phase.

We may demonstrate the principally exhibiting relationships by assuming that both solutions α and β behave ideally. Under these circumstances,

$$\bar{G}_{A(\alpha)}^{\text{mix}} = RT \ln x_{A(\alpha)}$$

$$\bar{G}_{A(\beta)}^{\text{mix}} = RT \ln x_{A(\beta)}$$

or

$$RT \ln \frac{x_{A(\alpha)}}{x_{A(\beta)}} = \Delta G_{A(\alpha \rightarrow \beta)}$$

and, analogously, for the component B:

$$RT \ln \frac{x_{B(\beta)}}{x_{B(\alpha)}} = \Delta G_{B(\beta \rightarrow \alpha)} \quad (5)$$

It is thus possible, from a knowledge of the transformation energies $\Delta G_{A(\alpha \rightarrow \beta)}$ and $\Delta G_{B(\beta \rightarrow \alpha)}$ and the solution behavior, to calculate the phase diagram; or to derive from experimentally established solubility data the quantities $\Delta G_{A(\alpha \rightarrow \beta)}$ and $\Delta G_{B(\beta \rightarrow \alpha)}$, i.e. the lattice stabilities of the components in modifications other than the stable ones.

For the case that $\Delta G_{A(\alpha \rightarrow \beta)} \gg \Delta G_{B(\beta \rightarrow \alpha)}$, the homogeneity range of the β -solution is negligibly small. Under these circumstances,

$$\bar{G}_{B(\beta)}^{\text{mix}} \approx 0,$$

and equation (4b) reduces to

$$-\bar{G}_{B(\alpha)}^{\text{mix}} = \Delta G_{B(\beta \rightarrow \alpha)} \quad (6)$$

For ideal solutions, this results in the simple relation

$$RT \ln x_{B(\alpha)} = - \Delta G_{B(\beta \rightarrow \alpha)}$$

or, since

$$\frac{\frac{\partial \Delta G_{B(\beta \rightarrow \alpha)}}{\partial T}}{T} = - \frac{1}{T^2} \frac{\partial \Delta H_{B(\beta \rightarrow \alpha)}}{\partial T}$$

in the familiar Clausius-Clapeyron-type of equation

$$\frac{\ln x_{B(\alpha)}}{T} = \frac{\Delta H_{B(\beta \rightarrow \alpha)}}{RT^2} \quad (7)$$

This relation, in the integrated form

$$\ln x = A - \frac{\Delta H}{T}$$

is commonly used to derive the enthalpy change ΔH from experimental solubility curves ("heats of solution").

In practice, ideal solution behavior is rarely found and the partial quantities have to be derived either from independently obtained thermochemical data, or deviations from ideality are accounted for by fitting suitable mathematical expressions to experimental phase diagram data. In many instances the regular solution approach^(1,2,9,10)

$$G = \sum \epsilon_{ij} x_i x_j + RT \sum x_i \ln x_i$$

is found satisfactory to approximate the actual behavior with sufficient accuracy.

Using the formulas discussed above and using the regular solution approach to account for deviations from ideal solutions behavior, the free enthalpy differences between the hexagonal close-packed (A3), the face-centered cubic (A2) modifications of molybdenum and tungsten have been derived from their binary systems with platinum metals and rhenium and are listed in Table 1. A compilation of the lattice stabilities of selected metals is provided in the work referenced under⁽¹¹⁾, and stabilities of high temperature carbide phases calculated from pseudobinary systems may be found in a previous publication.⁽⁹⁾

Table 1

Stabilities of Molybdenum and Tungsten in Different Crystal Modifications

Metal	$\Delta G_{\text{bcc} \rightarrow \text{hcp}}$ (cal/gr.-At)		$\Delta G_{\text{bcc} \rightarrow \text{fcc}}$ (cal/gr.-At)
	Ref.11	Ref.10	Ref.11
Mo	+ 2,000	+ 1,500	$2500 + 0.15 \cdot T$ (°K)
W	+ 2,000	+ 2,800	$2500 + 0.15 \cdot T$ (°K)

II. THERMOCHEMISTRY OF PHASE REACTIONS IN TERNARY SYSTEMS

According to Gibb's phase rule, the maximum number of phases which can coexist in a three component system is five, or, with temperature and pressure fixed, three. A temperature section of a ternary system will, therefore, ordinarily consist of an arrangement of one-, two-, and three-phase equilibria. Four-phase equilibria (four-phase temperature planes) are important in the melting ranges, but seldomly occur in the solid state. Nevertheless, the existence of four-phase temperature planes can be derived by considering the temperature of an additional variable, i.e., by analyzing a series of temperature sections. The mathematical approach thus concentrates on the establishment of the conditional equations for the two- and three-phase equilibria at constant temperature and pressure.

A. TWO-PHASE EQUILIBRIUM IN A TERNARY SYSTEM BETWEEN PHASES $[A_{x'}B_{y'}]C_{u'}$ - $[A_{x''}B_{y''}]C_{u''}$

A variation of the free energy in such a system is possible by exchanges of A and B on the (A,B) sublattices, and also by changing the overall

content of the component C (u' and u'') in the solid solution. For such a system, it is advantageous to base the calculations on one mole (A + B) instead on a gram atom as is conventionally done.

The free enthalpies of the two ternary phase solutions will then be expressible as ($T, p = \text{const}$)

$$G_1 = x'f_1(u') + y'\phi_1(u') + R_1(x', y') \quad (8a)$$

and

$$G_2 = x''f_2(u'') + y''\phi_2(u'') + R_2(x'', y'') \quad (8b)$$

$f_1(u')$ and $\phi_1(u')$ are the integral free enthalpies for phase 1 in the binary systems A-C and B-C, respectively, and $f_2(u'')$ and $\phi_2(u'')$ for phase 2. $R_1(x', y')$ and $R_2(x'', y'')$ are the free enthalpies of mixing on the sublattices (A, B) in both phases.

The equilibrium state, after Gibbs, is characterized by the condition that the thermodynamic potentials (partial free enthalpies) of each component are the same in both phases, i.e.

$$\bar{G}_{A(1)} = \bar{G}_{A(2)} \quad (9a)$$

$$\bar{G}_{B(1)} = \bar{G}_{B(2)} \quad (9b)$$

$$\bar{G}_{C(1)} = \bar{G}_{C(2)} \quad (9c)$$

whereby ($T, p = \text{const}$)

$$\bar{G}_A = G - y \left(\frac{\partial G}{\partial y} \right)_u - u \left(\frac{\partial G}{\partial u} \right)_x \quad (10a)$$

$$\bar{G}_B = G - x \left(\frac{\partial G}{\partial x} \right)_u - u \left(\frac{\partial G}{\partial u} \right)_x \quad (10b)$$

$$\bar{G}_C = \left(\frac{\partial G}{\partial u} \right)_x \quad (10c)$$

Together with the free enthalpy expressions (8a) and (8b) we obtain,

$$\bar{G}_{A(1)} = f_1(u') + \bar{G}_{A(1)}^{\text{mix}} - u' x' \left[\frac{\partial f_1(u')}{\partial u'} \right]_{x'} + y' \left[\frac{\partial \phi_1(u')}{\partial u'} \right]_{x'} \quad (11a)$$

$$\bar{G}_{B(1)} = \phi_1(u') + \bar{G}_{B(1)}^{\text{mix}} - u' x' \left[\frac{\partial f_1(u')}{\partial u'} \right]_{x'} + y' \left[\frac{\partial \phi_1(u')}{\partial u'} \right]_{x'} \quad (11b)$$

$$\bar{G}_{C(1)} = x' \left[\frac{\partial f_1(u')}{\partial u'} \right]_{x'} + y' \left[\frac{\partial \phi_1(u')}{\partial u'} \right]_{x'} \quad (11c)$$

and analogously,

$$\bar{G}_{A(2)} = f_2(u'') + \bar{G}_{A(2)}^{\text{mix}} - u'' x'' \left[\frac{\partial f_2(u'')}{\partial u''} \right]_{x''} + y'' \left[\frac{\partial \phi_2(u'')}{\partial u''} \right]_{x''} \quad (12a)$$

$$\bar{G}_{B(2)} = \phi_2(u'') + \bar{G}_{B(2)}^{\text{mix}} - u'' x'' \left[\frac{\partial f_2(u'')}{\partial u''} \right]_{x''} + y'' \left[\frac{\partial \phi_2(u'')}{\partial u''} \right]_{x''} \quad (12b)$$

$$\bar{G}_{C(2)} = x'' \left[\frac{\partial f_2(u'')}{\partial u''} \right]_{x''} + y'' \left[\frac{\partial \phi_2(u'')}{\partial u''} \right]_{x''} \quad (12c)$$

with

$$\bar{G}_{A(1)}^{\text{mix}} = R_1(x', y') + y' \cdot \frac{\partial R_1(x', y')}{\partial x'} \quad (13a)$$

$$\bar{G}_{B(1)}^{\text{mix}} = R_1(x', y') + x' \cdot \frac{\partial R_1(x', y')}{\partial y'} \quad (13b)$$

$$\bar{G}_{A(2)}^{\text{mix}} = R_2(x'', y'') + y'' \cdot \frac{\partial R_2(x'', y'')}{\partial x''} \quad (13c)$$

$$\bar{G}_{B(2)}^{\text{mix}} = R_2(x'', y'') + x'' \cdot \frac{\partial R_2(x'', y'')}{\partial y''} \quad (13d)$$

Equations (10) and (11) uniquely define the equilibrium state and permit evaluation of the equilibrium compositions of the phases. One concentration variable (either the gross composition, x' or x'') is chosen as a free parameter.

Although the resulting equations appear quite involved, they do allow a fairly straight-forward evaluation of the base points of the tie lines for the unrestricted case. ⁽¹²⁾

In many instances, however, considerable simplifications can be achieved by taking advantage of certain characteristics of the boundary systems and by substituting suitable expressions for the free enthalpies of the partaking phases. Thus, as found frequently, if u' and u'' can be considered as constants, it follows from (9) that a valid partial solution is also given by:

$$\bar{G}_{A(1)} - \bar{G}_{B(1)} = \bar{G}_{A(2)} - \bar{G}_{B(2)} \quad (14)$$

Inserting the partial quantities from equations (11) and (12) into (14), we obtain:

$$\bar{G}_{A(1)}^{\text{mix}} - \bar{G}_{B(1)}^{\text{mix}} - \bar{G}_{A(2)}^{\text{mix}} + \bar{G}_{B(2)}^{\text{mix}} = f_2(u'') - \phi_2(u'') + \phi_1(u'') - f_1(u') \quad (15)$$

or

$$\left(\frac{\partial G_1}{\partial x'} \right)_{T, p, u'} = \left(\frac{\partial G_2}{\partial x''} \right)_{T, p, u''} \quad (16)$$

G_1, G_2 = Integral free energies of formation of phase solutions 1 and 2.

Taking, as an illustration of the application of equation (15), the phase diagram example shown in Figure 2, we have ($u' = 0, u'' = 1, T, p = \text{const.}$)

$$f_1(u') = \Delta G_{f,A} = 0$$

$$f_2(u') = \Delta G_{f,B} = 0$$

$$\phi_1(u'') = \Delta G_{f,AC}$$

$$\phi_2(u'') = \Delta G_{f,BC}$$

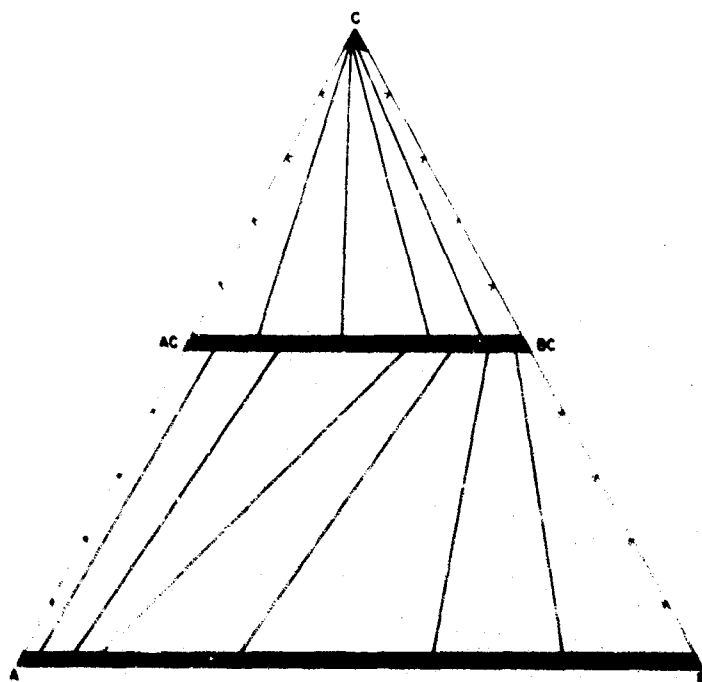


Figure 2. Appearance of Extended Two-Phase Fields in a System with Solid Solution Formation Between the Components and the Intermediate Phases.

$\Delta G_{f,i}$ = Free enthalpy of formation of phase i.

With
$$\bar{G}_i^{\text{mix}} = RT \ln a_i$$

a_iactivity of i = $f_i x_i$

we obtain from equation (15)

$$RT \ln \frac{a'_A}{a'_B} \cdot \frac{a''_B}{a''_A} = \Delta G_{f,AC} - \Delta G_{f,BC} \quad (17)$$

For ideal solutions ($a_i = x_i$)

$$RT \ln K = \Delta G_{f,AC} - \Delta G_{f,BC} \quad (18)$$

$$K = \frac{x'_A}{1-x'_A} \cdot \frac{1-x''_A}{x''_A}$$

From the known solution behavior, the differences of the free enthalpies of formation of the binary phases AC and BC can be determined from the experimental tie line distribution or, conversely, the tie line distribution in the two-phase field can be calculated from known free energy data.

We shall not discuss in any detail the effect of temperature and non-ideal solution behavior upon the tie line distribution in a two-phase field since this has been done elsewhere^(9,10), but instead concentrate on an actual example.

In the V-Mo-C system, the component metals, the subcarbides V_2C and Mo_2C , as well as the monocarbides VC_{1-x} and MoC_{1-x} at high temperatures, form complete series of solid solutions⁽¹³⁾. The compositions of the

coexisting phases (tie lines) were determined by lattice parameter measurements on samples located within the respective two-phase fields.

Figure 3 illustrates the method which was used in smoothing the experimental data. The upper section shows the plot of unit cell volumes of the Me_2C phases as determined by lattice parameter measurements on samples whose locations in the system are depicted in the center section. The lower section of Figure 3 contains the lattice parameter measured for the bcc metal phase. As can be seen from the curves drawn through the experimental points, the apparent lattice dimensions in the two-phased alloys differ from the parameter curves for the $(\text{V}, \text{Mo})_2\text{C}$ and the (V, Mo) -solid solution at the same metal exchange. The true compositions are obtained by the horizontal intercepts with the lattice parameters, or unit cell volume, curves for the (V, Mo) and the $(\text{V}, \text{Mo})_2\text{C}$ solid solution, such as shown for one sample P in Figure 3. The composition data thus obtained are transferred to the isothermal section (Figure 3 center) and the coexisting phase compositions connected by a straight line (tie line). The auxiliary curves (dash-dotted in Figure 3) refer to the locus of parameters at the boundaries of the opposite phase solution.

Having established experimentally the coexisting phases across the two-phase field, the next step involves computation of the "equilibrium constant" K according to equation (18); departure of K from constancy as the two-phase field is traversed would be indicative of an appreciable departure of the solution from ideality. For the two-phase equilibrium $(\text{V}, \text{Mo}) + (\text{V}, \text{Mo})_2\text{C}$, however, we find

$$K \pm 4.75 \pm 0.40,$$

the indicated error limits being well within the bounds set by the accuracy of the experimental data. [Compare the calculated tie lines (dashed curves) in Figure 3, and the $x'-x''$ plot in Figure 4.]

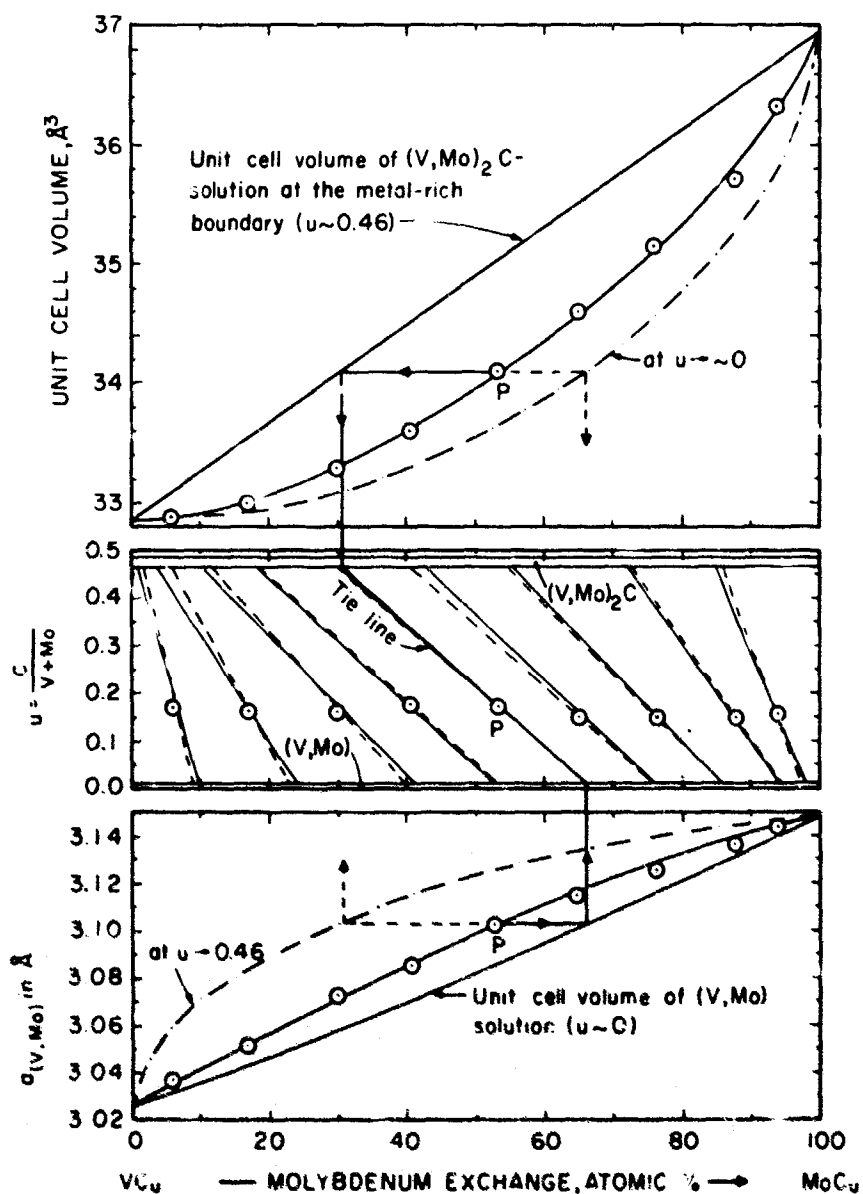


Figure 3. Determination of the Tie Line Distribution in the Two-Phase Field (V,Mo) + (V,Mo)₂C by Lattice Parameter Measurements on an Alloy Series at ~15 At. % C. Equilibration temperature 1230°C.

--- Calculated with $K = 4.75$

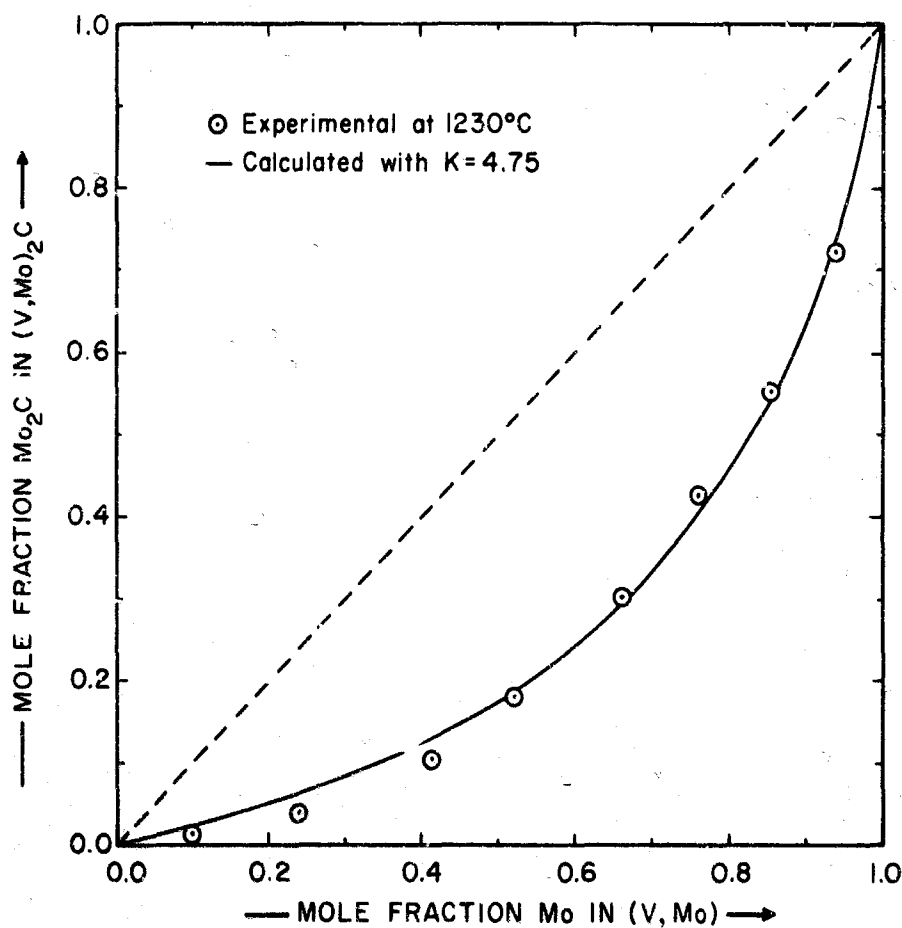


Figure 4. Plot of the Coexisting Metal and Subcarbide Solid Solutions in the V-Mo-C System at 1230°C.

The equilibrium constant K is thus related to the free enthalpies of formation of the subcarbide phases in the edge binaries V-C and Mo-C by

$$RT \ln K = \Delta G_{f, \text{MoC}_{1/2}} - \Delta G_{f, \text{VC}_{1/2}}$$

Insertion of temperature of $\sim 1500^\circ\text{K}$ and the above value for K yields

$$\Delta G_{f, \text{MoC}_{0.46}} - \Delta G_{f, \text{VC}_{0.46}} = 4640 \pm 400 \text{ cal/gr. At. Metal} \quad (19)$$

Experimental work carried out at 1800°K led to $K = 4.04 \pm 0.40$ for the same equilibrium, or a value for

$$\Delta G_{\text{MoC}_{0.45}} - \Delta G_{\text{VC}_{0.45}} = 5060 \pm 400 \text{ cal/gr. At. Metal} \quad (20)$$

The analysis of two-phase equilibria only yields differences for the free enthalpies; to obtain absolute quantities, the free enthalpy of formation of at least one of the boundary phases has to be known. In the foregoing example, the free energies of formation of Mo_2C appears quite well established, while that of V_2C is unknown. From the data compiled by Pankratz et al.⁽¹⁴⁾, $\Delta G_{f, \text{MoC}_{1/2}}$ can be approximated for the temperature range above 1400°K with sufficient accuracy by the expression

$$\Delta G_{f, \text{MoC}_{1/2}} = -1450 - 1.36 \cdot T [\text{cal/gr. -At. Mo}] \quad (21)$$

Together with the free enthalpy difference (20) one obtains for an equilibrium temperature of 1800°K

$$\Delta G_{f, \text{VC}} = -12,260 [\text{cal/gr. -At. V}]$$

This value is independently confirmed by experimental studies of the V-W-C system, where the thermodynamic analysis of the two-phase equilibrium $(\text{V}, \text{W}) + (\text{V}, \text{W})_2\text{C}$ led to an equilibrium constant of $K = 9.0$ at 1800°K and a free enthalpy difference of

$$\Delta G_{f, \text{WC}_{0.45}} - \Delta G_{f, \text{VC}_{0.45}} = 7850 [\text{cal/gr. -At. Metal}] \quad (22)$$

Chang in his compilation of thermochemical data on carbides⁽¹⁵⁾, gives

$$\Delta G_{f, \text{WC}_{1/2}} = -3150 - 0.62 \cdot T [\text{cal/gr. -At. W}]$$

which leads to

$$\Delta G_{f, VC_{0.48}} (1800^\circ K) = - 12,120 \text{ [cal/gr.-At.V]},$$

which is in excellent agreement with the value derived from the V-Mo-C system.

In conclusion to the discussion of two-phase equilibria, we shall outline on the already used example of the V-Mo-C system the reverse case, namely the calculation of the tie line distribution from known thermodynamic data.

According to equation (18) for the case of ideal solutions, the equilibrium constant K can be calculated directly from the known free enthalpy differences of the phases. For nonideal solution behavior, however, the relationships will be less explicit, and thus the equilibrium concentrations more difficult to obtain; for such cases the graphical method, leaning on relation (16), is to be given preference.

For the (V,Mo)-(V,Mo)₂C two-phase equilibrium, the free enthalpies of formation of the two solutions is given by

$$\Delta G_{f,(V,Mo)} = RT [x' \ln x' + (1-x') \ln (1-x')] \quad (23a)$$

$$\begin{aligned} \Delta G_{f,(V,Mo)C_{0.46}} = x'' \Delta G_{f,MoC_{0.46}} + (1-x'') \Delta G_{f,VC_{0.46}} + RT [x'' \ln x'' + \\ + (1-x'') \ln (1-x'')] \end{aligned} \quad (23b)$$

x' = mole fraction of Mo in the (V,Mo) solution

x'' = mole fraction of Mo in the (V,Mo) sublattice of the (V,Mo)₂C solid solution.

The gradients are then (T, p const)

$$\frac{\partial \Delta G_{f, (V, Mo)}}{\partial x'} = RT \ln \frac{x'}{1-x'} \quad (24a)$$

and

$$\frac{\partial \Delta G_{f, (V, Mo)C_{0.46}}}{\partial x''} = \Delta G_{f, MoC_{0.46}} - \Delta G_{f, VC_{0.46}} + RT \ln \frac{x''}{1-x''} \quad (24b)$$

These gradients, divided by $4.574 \cdot T$ are plotted against the concentration in Figure 5. As shown in this illustration, the tie lines, for any prechosen value of x' or x'' , are obtained as horizontal intercepts between both gradient curves, (Figure 5).

B. THREE-PHASE EQUILIBRIUM IN A TERNARY SYSTEM BETWEEN PHASES $(A_{x'}, B_{y'})C_u - (A_{x''}, B_{y''})C_v - (A_{x'''}, B_{y'''})C_w$

In essence, all types of three-phase equilibria occurring in a ternary system can be reduced to the two cases shown in Figures 6 and 7. Cases related to the one shown in Figure 7 are three-phase equilibria resulting from pseudobinary eutectic (eutectoid) or peritectic (peritectoid) reactions.

The general solution for the three-phase equilibrium represents the tangent points of all triple tangent planes to the free-enthalpy surfaces of the three partaking phases. The multiplicity of solutions is ∞ , and the solution for the equilibrium concentrations of each individual phase is of the form (p = const)

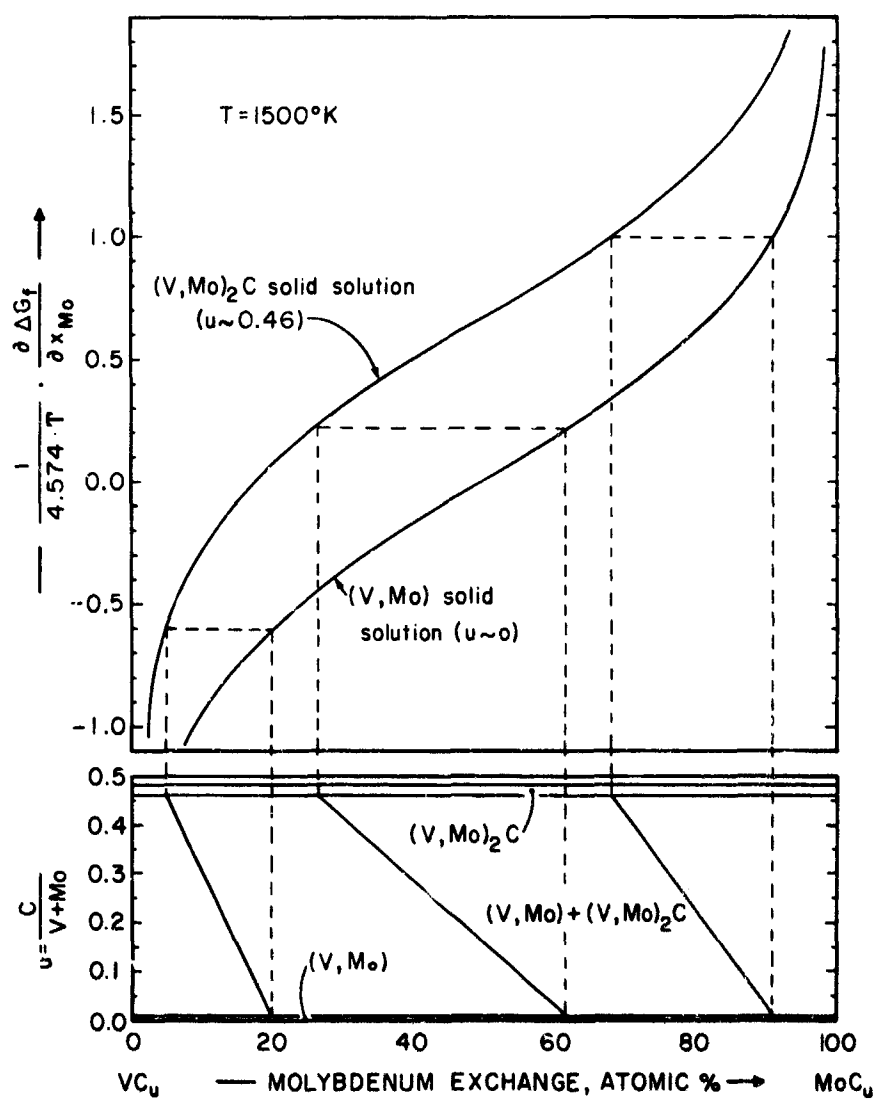


Figure 5. Graphical Determination of the Tie Line Distribution in the Two-Phase Field $(V, Mo) + (V, Mo)_2C$ at $1500^\circ K$.

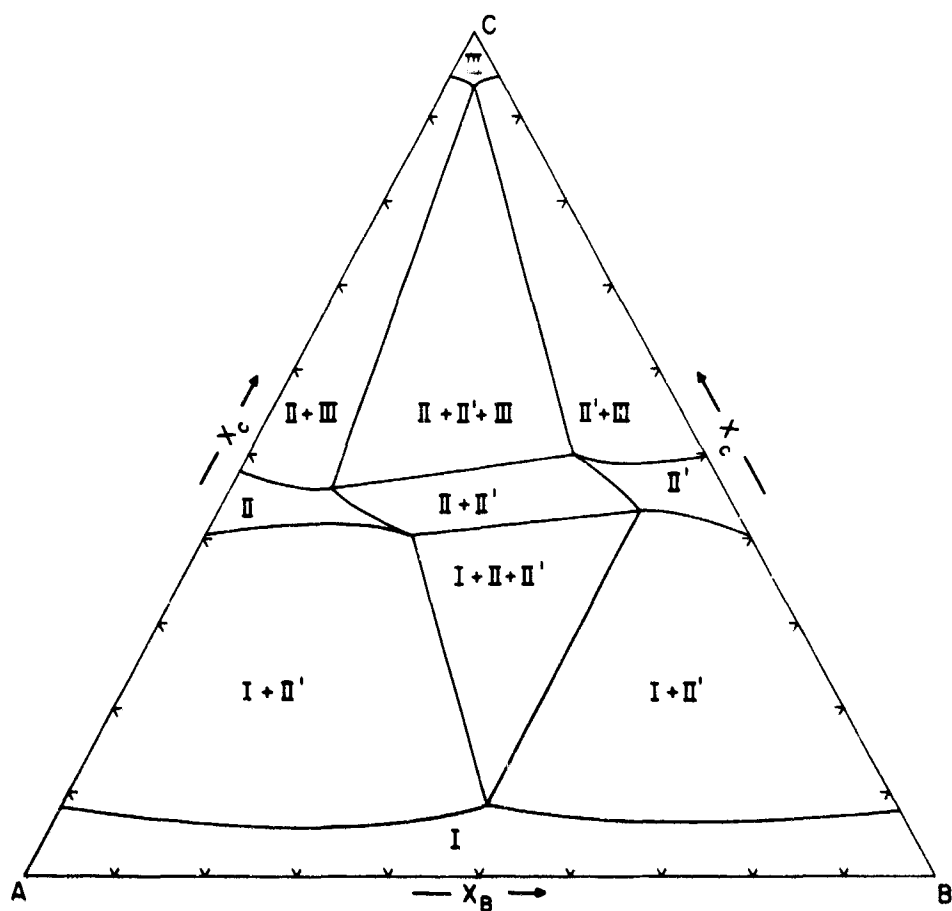


Figure 6. Three-Phase Equilibria Due to Formation of a Miscibility Gap in One of the Intermediate Phases.

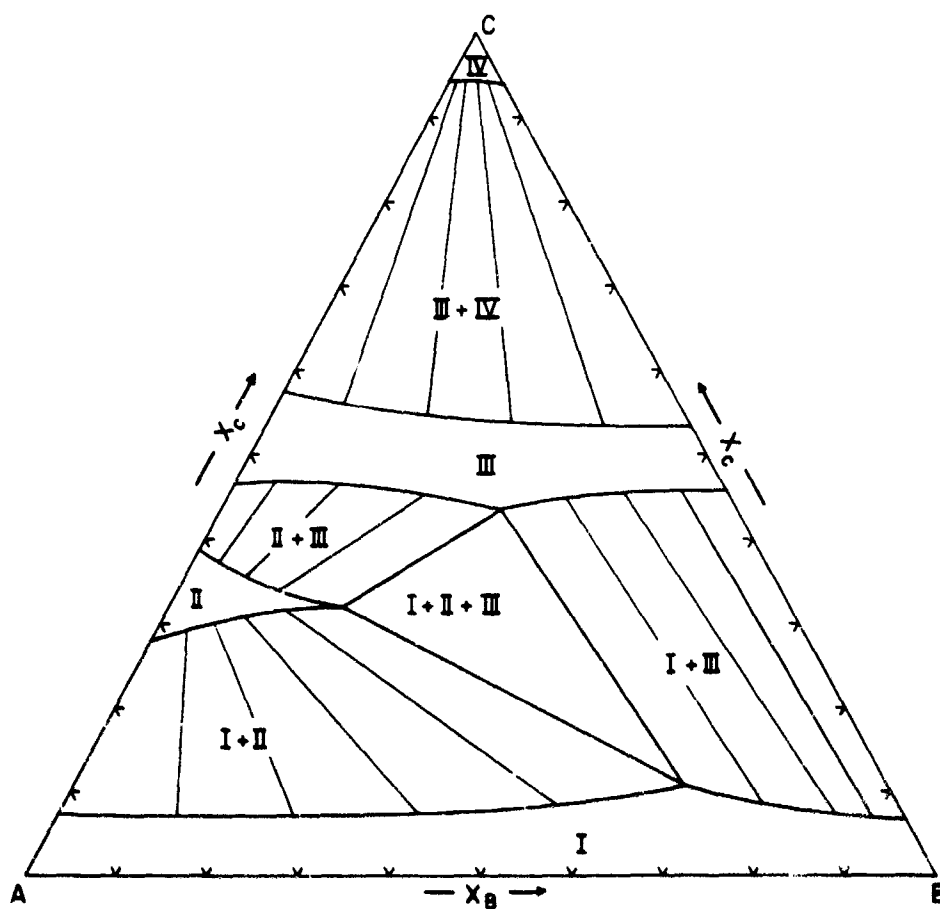


Figure 7. Termination of Phase II in a Three-Phase Equilibrium in the Ternary Owing to the Absence of an Isomorphous Counterphase in the B-C Binary.

$$\phi_1 (x_o, y_o, z_o, T) = 0$$

$$\phi_2 (x_o, y_o, z_o, T) = 0$$

$$(x_o + y_o + z_o = 1)$$

With $T = \text{const}$ (temperature sections), the concentrations are fixed and correspond to definite phase triplets (x_{oi}, y_{oi}, z_{oi}) .

For the numerical evaluation of the unrestricted problem, the general condition equation derived from the minimum condition and the existing constraints are only of limited use; the arithmetic in obtaining numerical solutions is quite involved, and, besides, the accuracy to which data concerning the variation of the free enthalpies across the homogeneity ranges of binary intermetallic phases are known at present, would not warrant highly detailed computations.

We thus introduce the same restrictions as done in the treatment of the ternary two-phase equilibrium, namely narrow, or constant, widths of the homogeneity ranges of the phases with respect to one of the components, and no atom interchange between the sublattices. An example representing these conditions is shown in Figure 8.

To derive the conditional equation for the three-phase equilibrium we consider an alloy with the gross composition $A_x B_y C_R$ to be composed of three phases,

$$v_1 \text{ moles } A_{x'} B_{y'} C_u \dots (\Delta G_1),$$

$$v_2 \text{ moles } A_{x''} B_{y''} C_v \dots (\Delta G_2)$$

$$v_3 \text{ moles } A_{x'''} B_{y'''} C_w \dots (\Delta G_3)$$

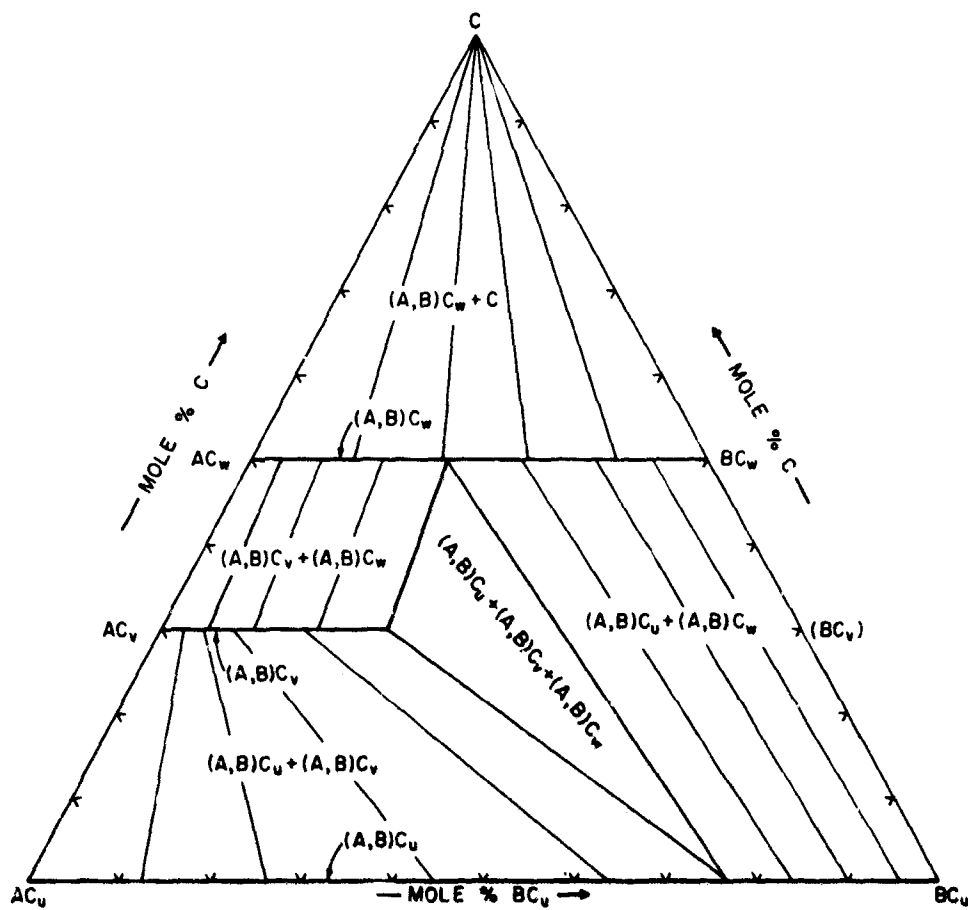


Figure 8. Ternary System of Phases Having Narrow Homogeneity Ranges with Respect to the Component C.

At constant temperature and pressure, the free enthalpy of the system is given by

$$\Delta G = v_1 \Delta G_1 + v_2 \Delta G_2 + v_3 \Delta G_3 \quad (25)$$

The equilibrium state is found by minimizing ΔG_2 under the given constraints, such as the conservation of the mole masses and the relations existing between the concentration variables. Determination of the extremum in the well known manner after Lagrange^(9,10) results in the conditional equations ($T, p = \text{const}$)

$$\frac{\partial \Delta G_1}{\partial x^I} = \frac{\partial \Delta G_2}{\partial x^{II}} = \frac{\partial \Delta G_3}{\partial x^{III}} \quad (26)$$

and

$$(v-w) \overline{\Delta G}_{BC_u} + (w-u) \overline{\Delta G}_{BC_v} + (u-v) \overline{\Delta G}_{BC_w} = 0 \quad (27a)$$

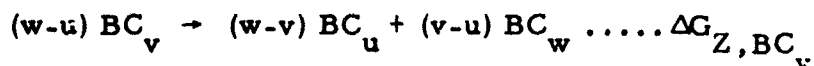
$$(v-w) \overline{\Delta G}_{AC_u} + (w-u) \overline{\Delta G}_{BC_v} + (u-v) \overline{\Delta G}_{BC_w} = 0 \quad (27b)$$

Equations (27), together with the conditional equation (26) for the three adjoining two-phase equilibria, uniquely define the equilibrium state. Equation (26) admits an infinite number of possible concentration triples of which the correct one, corresponding to the lowest free enthalpy, is sorted out with the aid of equation (27).

Separation of the partial free enthalpies in equation (27a) into base- and concentration dependent terms yields

$$\begin{aligned} & (v-w) \Delta G_{f,BC_u} + (w-u) \overline{\Delta G}_{f,BC_v} + (u-v) \overline{\Delta G}_{BC_w} + \\ & + (v-w) \overline{\Delta G}_{BC_u}^{\text{mix}} + (w-u) \overline{\Delta G}_{BC_v}^{\text{mix}} + (u-v) \overline{\Delta G}_{BC_w}^{\text{mix}} = 0 \end{aligned}$$

The first three terms correspond to the free enthalpy change of the reaction



and can be interpreted as the relative stability of BC_v in respect to the neighboring phases BC_u and BC_w . Analogously, we may regard the sum of the last three terms, containing the partial free enthalpies of mixing, as the corresponding free enthalpy change due to solid solution formation. Equation (27a) can therefore be rewritten to

$$\Delta G_{Z, BC_v} + \overline{\Delta G}_{Z, BC_v}^{\text{mix}} = 0 \quad (28a)$$

and, due to the reciprocity of the relations, equation (27b) to

$$\Delta G_{Z, AC_v} + \overline{\Delta G}_{Z, AC_v}^{\text{mix}} = 0 \quad (28b)$$

The three-phase equilibrium in a ternary system is, therefore, characterized by the condition, that the free enthalpies of disproportionation (relative stabilities) of the binary phases AC_v and BC_v are each brought to balance by the free enthalpy changes resulting from solid solution formation of the partaking phases. Relations (28a) and (28b) give us the means to separately determine the relative stabilities of AC_v and BC_v from experimental phase diagram data and known solution behavior, irrespective of the sign of $\Delta G_{Z, AC_v}$ ($\Delta G_{Z, BC_v}$), i.e. whether or not one of the phases exists as stable binary compound. This conclusion is important, since it allows us to obtain a definite number signifying how much a given compound in a binary is unstable in respect to the neighboring phases, and thus to determine its relative stability (Figure 9).

Relations (28a) and (28b) pertain to the equilibrium state. Any deviation from it will result in the appearance of a finite quantity, ϕ_Z , on the right-hand side, which, in essence, will be a measure of the imbalance between

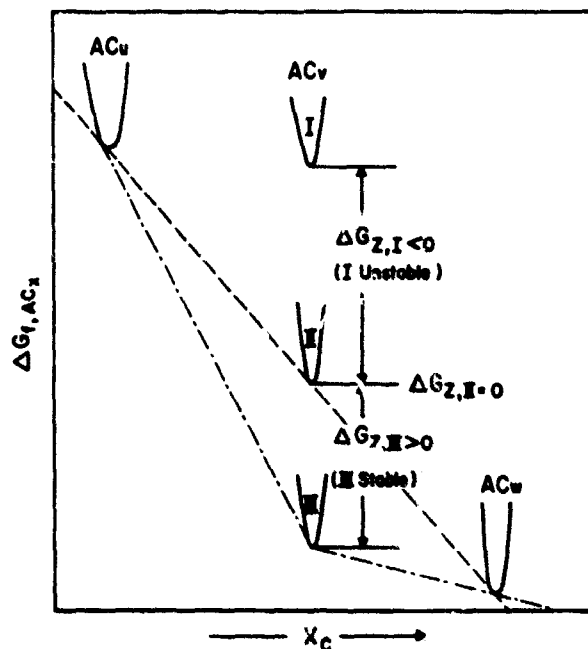


Figure 9. Stability Relationships in a Binary System A-C.

- I. Phase AC_v unstable in respect to a mechanical mixture of AC_u and AC_w ($\Delta G_{Z, AC_v} < 0$)
- II. Nonvariant equilibrium (stability limit of AC_v , $\Delta G_{Z, AC_v} = 0$)
- III. Phase AC_v stable ($\Delta G_{Z, AC_v} > 0$)

the disproportionation terms, ΔG_Z , for the binary compounds, and the corresponding mixing quantities. We may generalize equations (28) and write

$$\phi_{Z, AC_v} = \Delta G_{Z, AC_v} + \overline{\Delta G}_{Z, AC_v}^{\text{mix}} \quad (29a)$$

and

$$\phi_{Z, BC_v} = \Delta G_{Z, BC_v} + \overline{\Delta G}_{Z, BC_v}^{\text{mix}} \quad (29b)$$

and note that, at equilibrium, $\phi_Z = 0$.

For positive values of ϕ_Z , the solution $(A,B)C_v$ is stable in respect to mechanical mixtures of $(A,B)C_u$ and $(A,B)C_w$ whereas for negative values the solution $(A,B)C_v$ becomes unstable and disproportionates into mixtures of $(A,B)C_u$ and $(A,B)C_w$.

So far, our relations have dealt only with partial quantities and we therefore expect the functions ϕ_Z to describe the partial disproportionation quantities only. It can now be shown^(9,16) however, that the function ϕ_{Z,AC_v} and ϕ_{Z,BC_v} are identical and equal to the integral free enthalpy of disproportionation^v (relative stability) of the solution $(A,B)C_v$, viz.

$$\phi_{Z,(A,B)C_v} \equiv \phi_{Z,AC_v} \equiv \phi_{Z,BC_v}$$

We thus obtain the important result, that the integral free enthalpy of disproportionation (relative stability) of the solution $(A,B)C_v$ is equivalent to the sum of the free enthalpy of disproportionation of either of the binary phases, AC_v or BC_v , and the partial free energies of disproportionation for the same component.

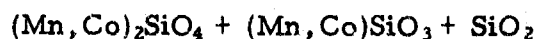
To determine the equilibrium concentrations from given thermodynamic data, we first employ the gradient condition, which yields the vertices of all coexisting phase triples possible for the entire range of exchanges (A,B) . These "compatible" concentration triples are then substituted into equations (29a) or (29b). The correct phase triple is the one for which ϕ_{Z,AC_v} , or ϕ_{Z,BC_v} , equals zero.

As outlined in the discussion of two-phase equilibria, the graphical method offers the most convenient route to evaluate the equations. A closed solution for ϕ_Z , which often is useful in initial estimates of the gross behavior of the phase relationships in a system, can only be obtained for the case that the solutions behave ideally.⁽⁹⁾

As an example for the application of the equations derived for two- and three-phase equilibria we select the 1250°C isotherm of the CoO-MnO-SiO₂ system recently investigated by Biggers and Muan⁽¹⁷⁾ (Figure 10). The tie line distribution in the two-phase fields were determined by lattice parameter measurements on two-phased, (Mn,Co)O + (Mn,Co)₂SiO₄ and (Mn,Co)₂SiO₄ + (Mn,Co)SiO₃, alloys which were homogenized at the chosen equilibrium temperature. In addition, activity-composition relations for the solid solutions were established by a gas-solid equilibration technique, and the instability of CoSiO₃ was derived from measurements of the CO/CO ratios of a gas phase coexisting with metallic cobalt, silica, and (Mn,Co)SiO₃ solutions. Their data showed, that the (Mn,Co)O and the metal silicate solution behave practically ideally, whereas the orthosilicate solution shows a slight negative departure.

With the exception of the monocarbide solid solution series and SiO₂, the phases in this system have three sublattices, that of oxygen, silicon, and of the metal component. Substitution occurs only in the metal sublattice and the boundary locations for a given solid solution in respect to SiO₂ are practically independent of the metal exchange.

It is seen from conditional equations (28) and (29) that the relative stabilities of the phases MnSiO₃ and CoSiO₃ are uniquely defined by the location of the vertices of the three-phase equilibrium



and the known solution behavior and that no independent experiments appear necessary for their determination.

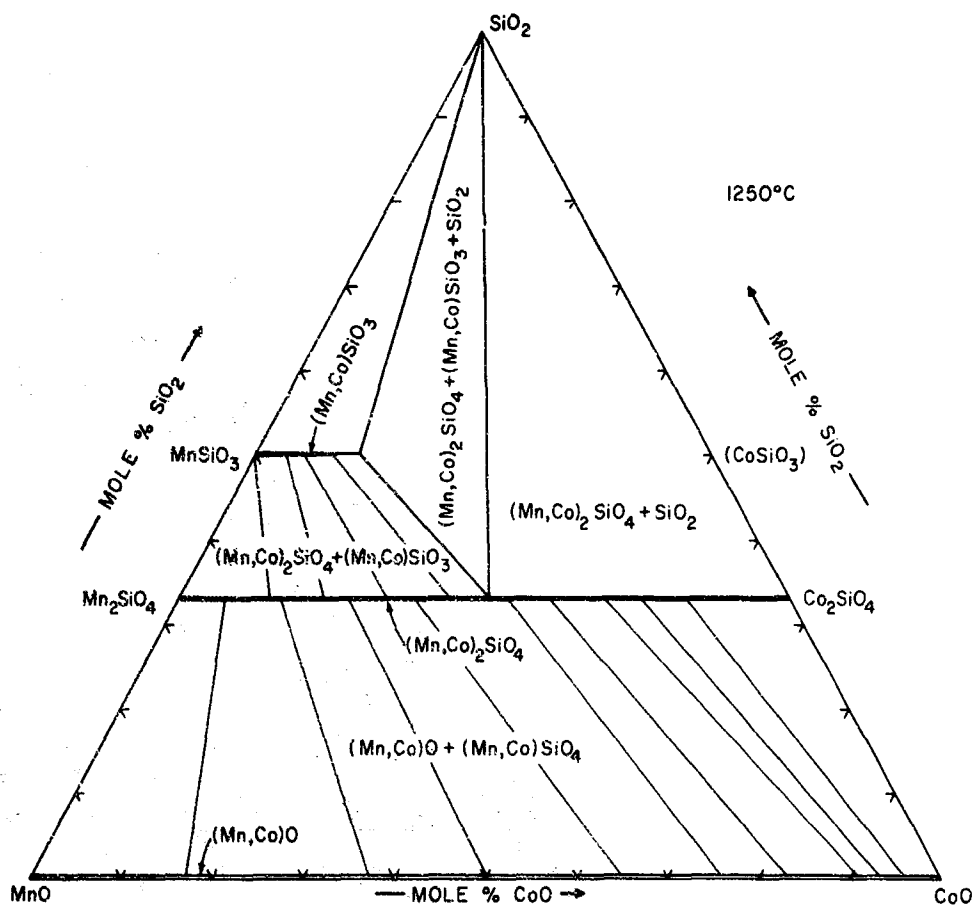


Figure 10. Isothermal Section of the MnO-CoO-SiO₂ System at 1250°C. (After Biggers and Muan, 1967).

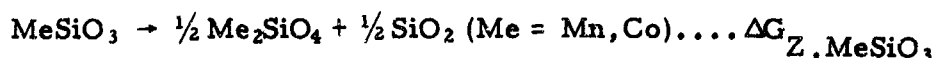
Stability condition (28), rewritten for the three-phase equilibrium in this system, becomes ($T, p = \text{const}$)

$$\Delta G_{Z, \text{CoSiO}_3} + \overline{\Delta G}_{Z, \text{CoSiO}_3}^{\text{mix}} = 0 \quad (30a)$$

and

$$\Delta G_{Z, \text{MnSiO}_3} + \overline{\Delta G}_{Z, \text{MnSiO}_3}^{\text{mix}} = 0 \quad (30b)$$

where $\Delta G_{Z, \text{CoSiO}_3}$ and $\Delta G_{Z, \text{MnSiO}_3}$ are the free enthalpies of disproportionation of the respective metasilicates into orthosilicate and SiO_2 according to



and the terms $\overline{\Delta G}_{Z, \text{MeSiO}_3}^{\text{mix}}$ include the partial free enthalpies of mixing of the boundary phases partaking in the equilibrium according to the same reaction scheme.

In these equations, the stoichiometry factors assume the values $u = \frac{1}{2}$, $v = 1$, and $w = \infty$ (negligible solubility of MnO and CoO in SiO_2).

Under these circumstances, equations (31) become

$$\Delta G_{Z, \text{MnSiO}_3} = RT \ln \frac{a_{\text{Mn}}^{\text{III}}}{a_{\text{Mn}}^{\text{II}}} \quad (31a)$$

and

$$\Delta G_{Z, \text{CoSiO}_3} = RT \ln \frac{a_{\text{Co}}^{\text{III}}}{a_{\text{Co}}^{\text{II}}} \quad (31b)$$

$a_{\text{Mn}(\text{Co})}^{\text{II}}$ Activity of $\text{Mn}(\text{Co})_2\text{SiO}$ in the solid solution
($\text{Mn, Co})_2\text{SiO}$ relative to the pure binary compounds.

$a_{\text{Mn}(\text{Co})}^{\text{III}}$ Activity of $\text{Mn}(\text{Co})\text{SiO}_3$ in the solid solution
($\text{Mn, Co})\text{SiO}_3$ relative to the pure binary compounds

With $a_{\text{Co}}^{\text{II}} = 0.47$ ($x_{\text{Co}}^{\text{II}} = 0.51$), and $x_{\text{Co}}^{\text{III}} = a_{\text{Co}}^{\text{III}} = 0.24$, and an equilibrium temperature of 1523°K , equations (31a) and (31b) yield values of

$$\Delta G_{Z, \text{CoSiO}_3} = -2035 \text{ [cal/gr.-At. Co]}$$

and

$$\Delta G_{Z, MnSiO} = +1450 \text{ [cal/gr. -At. Mn]}$$

Considering the uncertainties of the experimental investigation, these values are only insignificantly different from $\Delta G_{Z, CoSiO_3} = -2280$ and $\Delta G_{Z, MnSiO_3} = +1320$ cal per gr. -At. metal calculated under the assumption of ideal solution behavior ($a'' = x''$). The above value of $\Delta G_{Z, CoSiO_3} = -2035$ cal per gr. -At. Co compares favorably with a value of -1900 cal derived by the cited authors⁽¹⁷⁾ from data gained by an independent equilibration experiment.

Using the accepted value of -2800 cal per gr. -At. Co for the free enthalpy of formation of Co_2SiO_4 from the oxide components⁽¹⁷⁾, the free enthalpies of formation of all other phases can be derived from the existing two- and three-phase equilibria in the system.

Thus, evaluation of the two-phase equilibrium $(Mn, Co)O + (Mn, Co)_2SiO_4$ yields (1250° C)

$$\Delta G_{f, Co_2SiO_4} - \Delta G_{f, Mn_2SiO_4} = 7300 \text{ cal per gr. -At. Metal,}$$

and the equilibrium $(Mn, Co)_2SiO_4 + (Mn, Co)SiO_3$,

$$\Delta G_{f, CoSiO_3} - \Delta G_{f, MnSiO_3} + \frac{1}{2}(\Delta G_{f, Mn_2SiO_4} - \Delta G_{f, Co_2SiO_4}) = 3820 \text{ cal per gr. -At. Metal}$$

Together with the data for $\Delta G_{Z, CoSiO_3}$ and $\Delta G_{Z, MnSiO_3}$ free enthalpy values compiled in Table 2 were derived. Although the interconsistency of the thermodynamic data calculated from the phase relationships in the system $MnO-CoO-SiO_2$ appears to be very good and are also in good agreement with the quantities derived from the cobalt precipitation experiments by the cited authors⁽¹⁷⁾, data calculated from related systems appear considerably at variance. Thus, taking

Table 2. Free Enthalpies of Formation of Manganese and Cobalt Silicates from the Oxide Components. Data Derived from Experimental Phase Relationships in the MnO-CoO-SiO₂ System at 1250°C

Reaction	Free Enthalpy Change at 1250°C
$2 \text{ CoO} + \text{SiO}_2 \rightarrow \text{Co}_2\text{SiO}_4$	$\Delta G_{f, \text{Co}_2\text{SiO}_4} = - 2800 \text{ cal/mole}^{(*)}$
$\text{CoO} + \text{SiO}_2 \rightarrow \text{CoSiO}_3$	$\Delta G_{f, \text{CoSiO}_3} = + 640 \text{ cal/mole}$
$2\text{MnO} + \text{SiO}_2 \rightarrow \text{Mn}_2\text{SiO}_4$	$\Delta G_{f, \text{Mn}_2\text{SiO}_4} = - 10,100 \text{ cal/mole}$
$\text{MnO} + \text{SiO}_2 \rightarrow \text{MnSiO}_3$	$\Delta G_{f, \text{MnSiO}_3} = - 6500 \text{ cal/mole}$

(*) Reference value for the calculation of the thermodynamic quantities for the other silicates.

the activities at the vertices of the three-phase equilibrium $(\text{Mn, Fe})_2\text{SiO}_4 + (\text{Mn, Fe})\text{SiO}_3 + \text{SiO}_2$ in the FeO-MnO-SiO₂ System⁽¹⁸⁾, one derives for $\Delta G_{Z, \text{MnSiO}_3} = + 640 \text{ cal}$ at 1150°C, as opposed to + 1450 cal obtained from the MnO-CoO-SiO₂ system. Since this disagreement is well outside the error range to be expected from unknown variations in the solid solution behavior, one is led to believe that the discrepancies very likely are to be attributed to inaccuracies in the determination of the phase equilibria.

We shall now demonstrate on the example of the MnO-CoO-SiO₂ system the use of the previously derived relations in the precalculation of phase relationships in the system MnO-CoO-SiO₂. For the sake of simplicity, we shall perform the calculations by assuming ideal solution behavior for all phases in the system. As input data we use the values derived from the experimental phase data which would be obtained if the solutions were treated ideally, namely:

$$\Delta G_{f, \text{Co}_2\text{SiO}_4} = -2800 \text{ cal/mole (reference value)}$$

$$\Delta G_{f, \text{Mn}_2\text{SiO}_4} = -9040 \text{ cal/mole}$$

$$\Delta G_{f, \text{MnSiO}_3} = -5850 \text{ cal/mole}$$

$$\Delta G_{f, \text{CoSiO}_3} = + 800 \text{ cal/mole}$$

The first step entails the establishment of the free enthalpy-concentration gradient curves according to conditional equation (16). For the solid solution (Mn,Co)O we have (T, p = const)

$$\Delta G_{f, (\text{Mn}, \text{Co})\text{O}} = RT [x'_{\text{Co}} \ln x'_{\text{Co}} + (1-x'_{\text{Co}}) \ln (1-x'_{\text{Co}})]$$

and

$$\frac{1}{4.574 \cdot T} \left[\frac{\partial \Delta G_{f, (\text{Mn}, \text{Co})\text{O}}}{\partial x'_{\text{Co}}} \right] = \frac{x'_{\text{Co}}}{1-x'_{\text{Co}}}$$

and for the (Mn,Co)₂SiO₃ -phase,

$$\begin{aligned} \Delta G_{f, (\text{Mn}, \text{Co})\text{Si}_{0.5}\text{O}_2} &= x''_{\text{Co}} \cdot \Delta G_{f, \text{CoSi}_{0.5}\text{O}_2} + (1-x''_{\text{Co}}) \cdot \Delta G_{f, \text{MnSi}_{0.5}\text{O}_2} + \\ &+ RT [x''_{\text{Co}} \ln x''_{\text{Co}} + (1-x''_{\text{Co}}) \ln (1-x''_{\text{Co}})] \end{aligned}$$

and

$$\frac{1}{4.574 \cdot T} \left[\frac{\partial \Delta G_{f, (\text{Mn}, \text{Co})\text{Si}_{0.5}\text{O}_2}}{\partial x''_{\text{Co}}} \right] = \frac{\Delta G_{f, \text{CoSi}_{0.5}\text{O}_2} - \Delta G_{f, \text{MnSi}_{0.5}\text{O}_2}}{4.574 \cdot T} + \log \frac{x''_{\text{Co}}}{1-x''_{\text{Co}}}$$

For the solid solution (Mn,Co)SiO₃ we obtain in an analogous manner:

$$\frac{1}{4.574 \cdot T} \left[\frac{\partial \Delta G_{f, (Mn, Co)SiO_3}}{\partial x'''_{Co}} \right] = \frac{\Delta G_{f, CoSiO_3} - \Delta G_{f, MnSiO_3}}{4.574 \cdot T} + \log \frac{x'''_{Co}}{1-x'''_{Co}}$$

Substitution of the free enthalpy quantities into the last two expressions and an equilibrium temperature of 1523°K yields the equations

$$\frac{1}{4.574 \cdot T} \left[\frac{\partial \Delta G_{f, (Mn, Co)Si_{0.5}O_2}}{\partial x''_{Co}} \right] = 0.4487 + \log \frac{x''_{Co}}{1-x''_{Co}}$$

and

$$\frac{1}{4.574 \cdot T} \left[\frac{\partial \Delta G_{f, (Mn, Co)SiO_3}}{\partial x'''_{Co}} \right] = 0.966 + \log \frac{x'''_{Co}}{1-x'''_{Co}}$$

These gradients are shown in graphical form in Figure 11 and are used to obtain the compositions of the coexisting phases in the two-phase fields.

To locate the vertices of the terminating three-phase equilibrium for the metasilicate solid solution we have to determine its relative stability in regard to mechanical mixtures of orthosilicate solution and SiO₂ (equation 29).

$$\begin{aligned} \phi_{Z, (Mn, Co)SiO_3} &= \Delta G_{Z, CoSiO_3} + RT \ln \frac{x''_{Co}}{x'''_{Co}} \\ &= \Delta G_{Z, MnSiO_3} + RT \ln \frac{1-x''_{Co}}{1-x'''_{Co}} \end{aligned}$$

According to our definition of the Z-quantities

$$\Delta G_{Z, CoSiO_3} = \frac{1}{2} \Delta G_{f, Co_2SiO_4} - \Delta G_{f, CoSiO_3}$$

or,

$$\Delta G_{Z, \text{CoSiO}_3} = -1400 - 880 = -2280 \text{ cal per gr.-At. Co}$$

and

$$\Delta G_{Z, \text{MnSiO}_3} = 1300 \text{ cal per gr.-At. Mn}$$

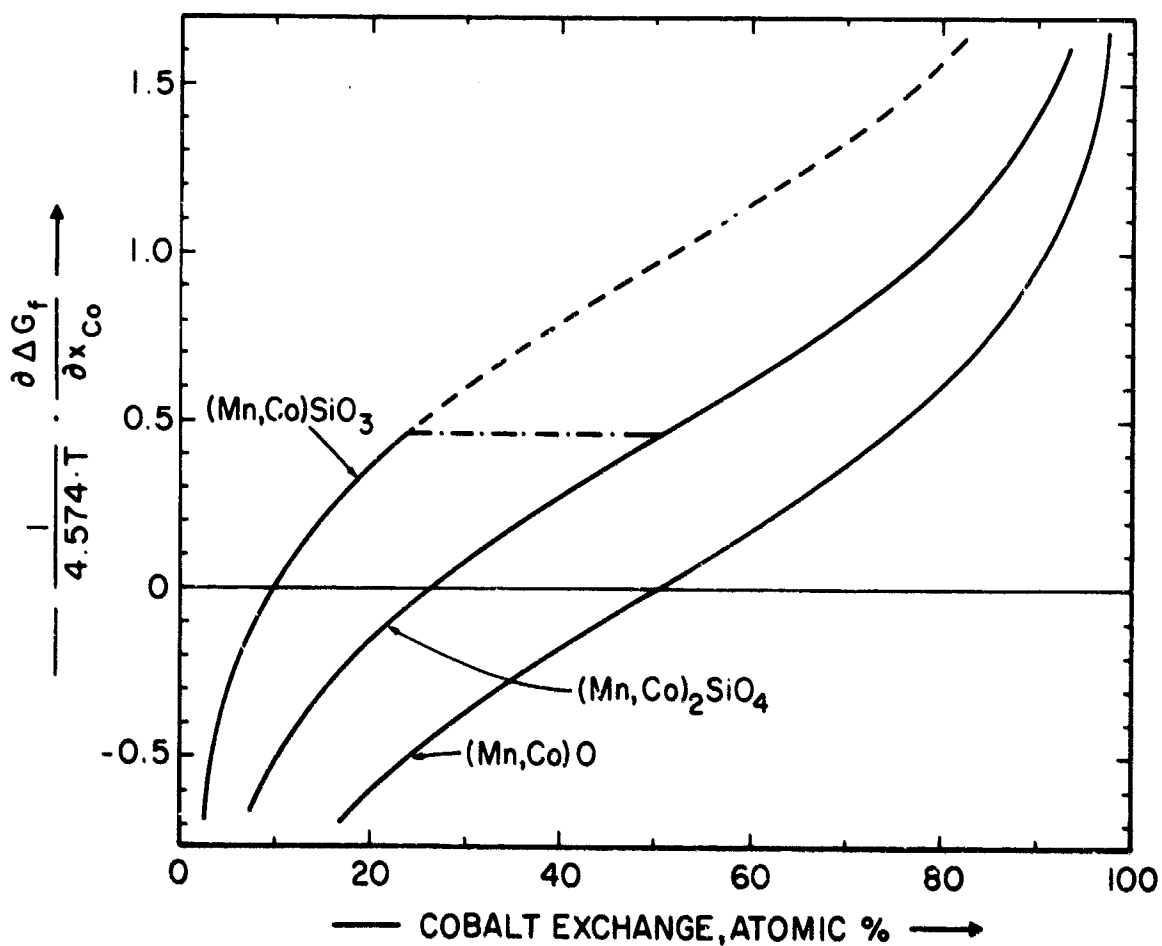


Figure 11. Free Enthalpy - Concentration Gradients for the Phase Solutions in the MnO-CoO-SiO₂ System (Ideal Solutions, T = 1523°K)

Dash-Dot Curve: Boundary tie line of the two-phase equilibrium (Mn,Co)SiO₃ + SiO₂

The function $\phi_{Z, (Mn, Co)SiO_3}$ is plotted in Figure 12 against the cobalt exchange (x'''_{Co}) in the metasilicate phase. Per definition, ϕ_Z at $x'''_{Co} = 0$ and $x'''_{Co} = 1$ correspond to the free enthalpies of disproportionation of the pure phases in the edge systems. We see from the plot, that the relative stability of the metasilicate solution rapidly decreases with increasing cobalt content until, at about $x'''_{Co} = 0.23$, it crosses the zero line, indicating that the stability limit of the (single-phased) solution has been reached. At still higher cobalt contents, the metasilicate solution is unstable in respect to mixtures of orthosilicate and SiO_2 .

The compositions of the coexisting phases are found from the gradient curves in Figure 11. The horizontal intercept with the gradient curve of the orthosilicate solution yields the vertex at the $(Mn, Co)_2SiO_4$ -phase ($x''_{Co} = 0.51$). According to our assumption of very limited solubilities in SiO_2 , the third vertex, of course, lies in the SiO_2 -corner. The temperature section of the system, assembled from the calculated composition data is shown in Figure 13.

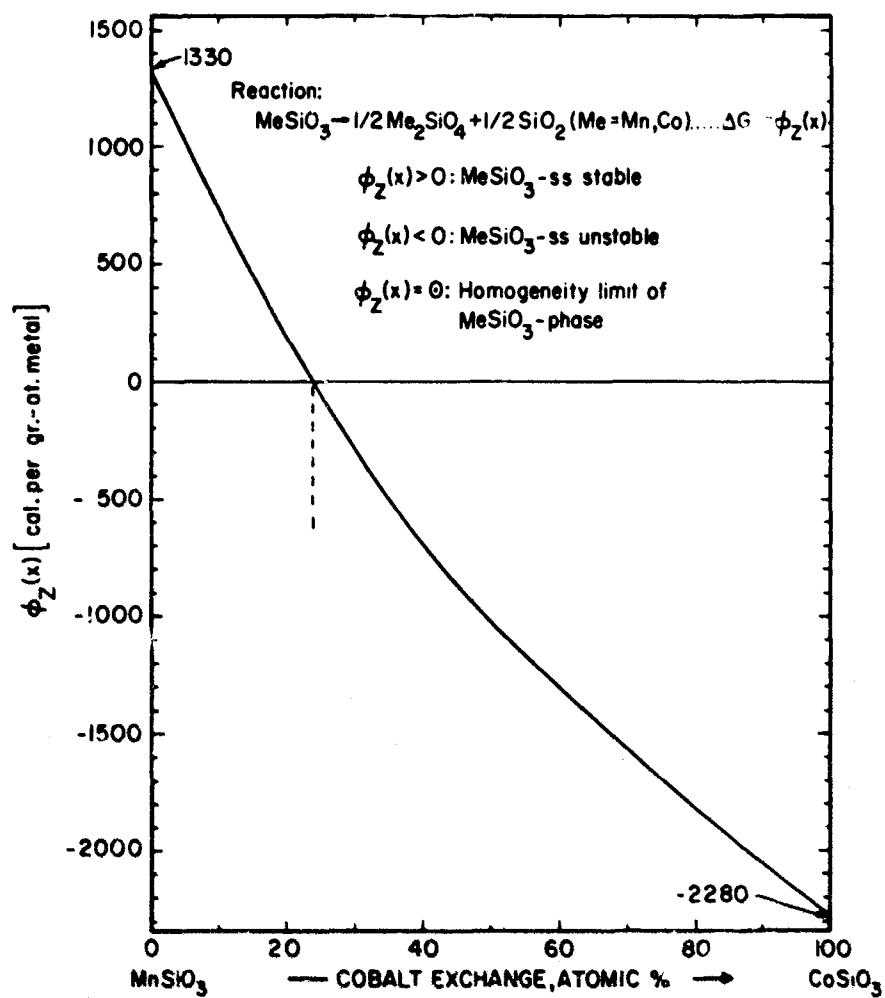


Figure 12. Integral Free Enthalpy of Disproportionation of the Metasilicate, $(\text{Mn,Co})\text{SiO}_3$, phase into Orthosilicate, $(\text{Mn,Co})_2\text{SiO}_4$, and SiO_2 .

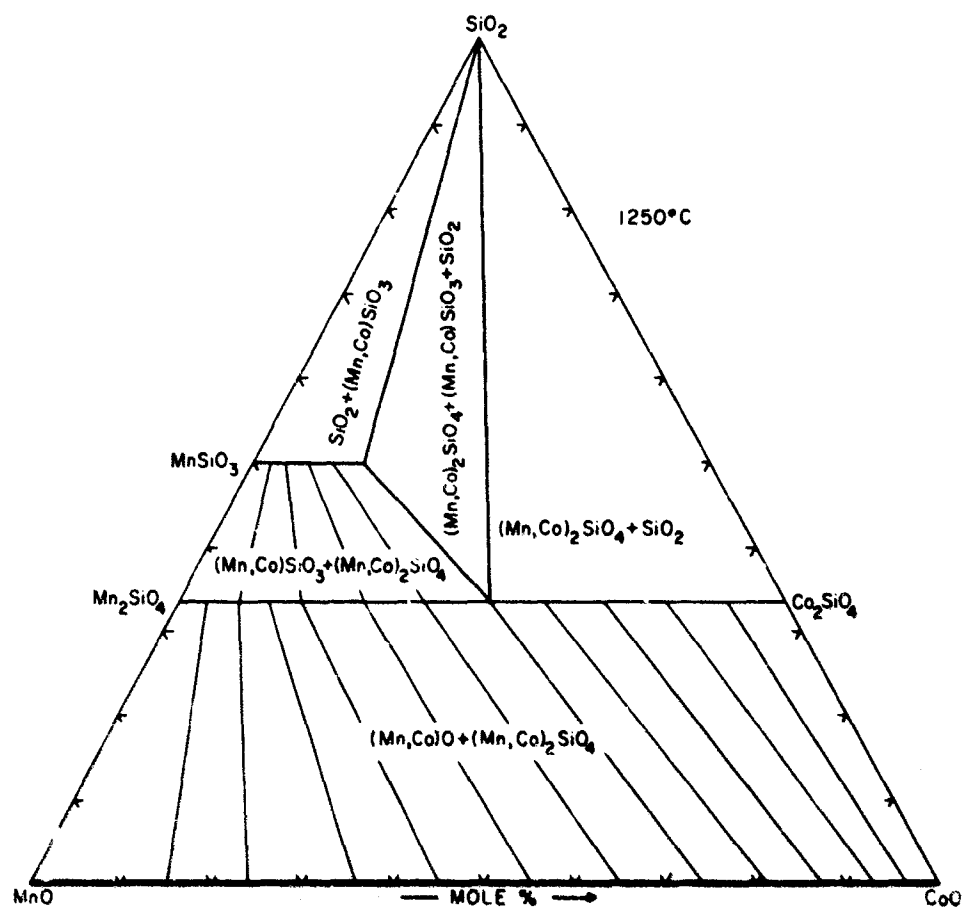


Figure 13. Calculated Isothermal Section of the MnO-CoO-SiO₂ System at 1250°C.

III. DISCUSSION

Although the systems treated in this report represent fairly simple cases, the approach taken in the computation of more complex ternaries is analogous and only the arithmetic becomes more laborious. Similarly, non-ideal solution behavior can be taken into account without increasing the complexity of the calculations.⁽¹⁰⁾

The most serious handicap in predicting phase equilibria concerns the fact that, to carry out the calculations, the free energy of formation of all phases in all structure types occurring in the particular system must be known. Since the thermodynamic stability of hypothetical phases principally cannot be measured by direct means, a certain amount of experimental phase studies, or other equilibration experiments, leading to the required data, appears indispensable. Once such data have been established for a particular alloy class from experimental phase studies on selected systems, the phase behavior in other systems belonging to the same class can be predicted. A considerable amount of work in this respect has been performed on ternary metal-carbon systems in which now, by virtue of a detailed thermodynamic interpretation carried out simultaneously with the experimental studies, the occurring phase equilibria and their temperature dependence are well understood.⁽¹⁹⁾

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13. ABSTRACT <p>The thermodynamic fundamentals relating phase equilibria in binary and ternary systems to the thermodynamic properties of the phases are reviewed and discussed. Considered in detail are partition equilibria in ternary systems and the role of the three-phase equilibrium in the determination of the relative stabilities of stable as well as hypothetical phases.</p> <p>Sample calculations carried out on selected ternary metal-carbon and a metal silicate system demonstrate the application of the equations for extracting thermodynamic data from phase diagrams and also for the prediction of phase equilibria.</p>		

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